

Membrane pinning on a disordered substrate

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Abstract

We investigate interactions between an elastic membrane and a substrate characterized by quenched positional disorder in the height function. We show that the positional disorder transforms the standard secondary DLVO minimum into two separate states: the hovering state characterized by a planar membrane at a finite separation from the interface and a pinned state where the membrane follows closely the asperities of the substrate and is as a consequence quite corrugated. The transition between the two states is continuous and depends on the parameters of the underlying DLVO potential as well as the parameters describing the quenched height-height correlation function of the substrate.

pac87.16.DgMembranes, bilayers, and vesicles pac8.15.+eLiquid thin films

In the DLVO theory one usually assumes that when a membrane or in general an elastic manifold interacts with a rigid substrate, the membrane is modelled as flat and the substrate is envisioned as featureless [1]. This leads in a straightforward manner to the secondary minimum of the DLVO theory and to an equilibrium spacing between the membrane and the substrate. Taking into account the elastic degrees of freedom of a membrane can alter this picture drastically, leading to the emergence of Helfrich interaction which may induce an unbinding transition of the membrane. This transition has been clearly shown to be a consequence of the interplay between elastic fluctuations of the membrane and DLVO interactions between the membrane and the substrate [2]. In the present work we are motivated by recent experiments on deposited lipid multilayers on atomically smooth vs. rough surfaces [3].

These experiments reveal differences in equilibrium lamellar spacings of lipid multilayers in proximity of a substrate that seem to correlate with molecular roughness of the substrate [3]. In order to lay ground for understanding effects of this type it is desirable to relax the

model constraint of a featureless substrate and treat it supposedly more realistically as exhibiting (quenched) disorder in the height function. We will analyze the consequences of this new model of a substrate interacting with a membrane and show that it modifies the simplified DLVO conclusions in the sense that the original secondary DLVO minimum now splits into two separate states, characterised by the way the membrane is (de)coupled to the substrate. We call these states the *hovering state* and the *pinned state*. The former one is characterized by a membrane in a flat configuration hovering a certain finite distance above the substrate and is directly related to the standard DLVO secondary minimum. The latter one is characterized by a corrugated membrane that basically follows the asperities of the quenched positional disorder of the substrate and is altogether missing from the standard DLVO theory. We stress that our description is unifying in the sense that it combines aspects of *mean-field* theory [6], which focuses on the nature of the pinned state; and a straight-forward generalization [4] of Li and Kardar's [5] *Gaussian fluctuation theory*, which allows for a hovering state determined by the parameters of the DLVO interaction potential. Specifically, we find that for sufficiently strong disorder, the membrane indeed prefers the mean-field pinned state considered by Swain and Andelman. Because of the increased role of substrate disorder fluctuations, in weakly disordered systems the properly self averaged free energy can give way to a hovering state where the membrane is depinned, residing in a minimum related to but different from the usual DLVO minimum, as predicted by Gaussian fluctuation theory.

We introduce our approach by first specifying the model of the membrane and the substrate that interact *via* a DLVO potential with (for matters of convenience) hydration and van der Waals terms. Formally our analysis owes a lot to investigations of effects of the disorder on polymerized membranes that have been analyzed in a variety of contexts [8]. It is based on the assumption of a Gaussian substrate height distribution function and the application of the $1/d$ expansion method ¹ to evaluate the complicated partition function stemming from the replicated Hamiltonian.

The Hamiltonian of a flexible membrane described in the usual Monge parameterization $u(\boldsymbol{\rho})$, where $\boldsymbol{\rho} = (x, y)$ is a 2D coordinate vector, above a substrate characterized by the height function $\zeta(\boldsymbol{\rho})$, where $\zeta(\boldsymbol{\rho})$ is a quenched disorder field describing the profile of the substrate, is composed of three contributions. First of all we have the elastic energy of the membrane, then the interaction free energy per unit surface area between the membrane and the substrate $V(u(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho}))$ of the general DLVO form, and finally the free energy contribution of an external force per unit surface area π pushing the membrane towards the substrate. The total free energy or equivalently the mesoscopic Hamiltonian thus assumes the form

$$\mathcal{H}[u(\boldsymbol{\rho})] = \frac{1}{2} \iint d^2 \boldsymbol{\rho} d^2 \boldsymbol{\rho}' \mathcal{K}(\boldsymbol{\rho}, \boldsymbol{\rho}') u(\boldsymbol{\rho}) u(\boldsymbol{\rho}') + \int d^2 \boldsymbol{\rho} V(u(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho})) + \int d^2 \boldsymbol{\rho} \pi (u(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho})).$$

Usually one takes for the elastic part the classical Canham - Helfrich - Evans *ansatz* $\mathcal{K}(\boldsymbol{\rho}, \boldsymbol{\rho}') = \nabla^4 K_c \delta^2(\boldsymbol{\rho} - \boldsymbol{\rho}')$, where K_c is the bending modulus of the membrane, while the

¹Strictly speaking what we use is actually a $1/(d - 2)$ expansion.

interaction part is composed of the attractive and repulsive DLVO ingredients. Since the interaction part of the Hamiltonian is in general non-linear it is convenient to introduce the following new variable $B(\boldsymbol{\rho}) = (u(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho}))^2$ at every $\boldsymbol{\rho}$ via a functional constraint [9]

$$\delta\mathcal{H}[B(\boldsymbol{\rho}), g(\boldsymbol{\rho})] = \frac{1}{2} \int d^2\boldsymbol{\rho} g(\boldsymbol{\rho}) ((u(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho}))^2 - B(\boldsymbol{\rho})).$$

Clearly the auxiliary field $g(\boldsymbol{\rho})$ plays a role akin to the self-energy part of the Green function. The two auxiliary fields $B(\boldsymbol{\rho})$ and $g(\boldsymbol{\rho})$ just introduced, play the role of fixing the local constraint $(u(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho}))^2 = B(\boldsymbol{\rho})$. They also show up in the partition function where one has to eventually take the trace over these auxiliary fields together with $u(\boldsymbol{\rho})$. The partition function can thus be written as

$$\mathcal{Z}[\zeta(\boldsymbol{\rho})] = \int \mathcal{D}u(\boldsymbol{\rho}) \mathcal{D}B(\boldsymbol{\rho}) \mathcal{D}g(\boldsymbol{\rho}) e^{-\beta(\mathcal{H}[u(\boldsymbol{\rho})] + \delta\mathcal{H}[B(\boldsymbol{\rho}), g(\boldsymbol{\rho})])}.$$

The average over the quenched disorder distribution, assuming the self-averaging property of the free energy, is defined to be of the form

$$\overline{(\dots)} = \int \mathcal{D}\zeta(\boldsymbol{\rho}) (\dots) \mathcal{P}[\zeta(\boldsymbol{\rho})],$$

where by assumption the disorder probability distribution function $\mathcal{P}(\zeta(\boldsymbol{\rho}))$ that characterises the quenched disorder in the height function of the substrate is given by a Gaussian *ansatz*

$$\mathcal{P}[\zeta(\boldsymbol{\rho})] = \exp\left(-\frac{1}{2} \iint d^2\boldsymbol{\rho} d^2\boldsymbol{\rho}' \mathcal{G}(\boldsymbol{\rho}, \boldsymbol{\rho}') \zeta(\boldsymbol{\rho}) \zeta(\boldsymbol{\rho}')\right).$$

The free energy, after being averaged also over the quenched disorder distribution, is obtained finally as

$$\mathcal{F} = -kT \overline{\log \mathcal{Z}[\zeta(\boldsymbol{\rho})]} = -kT \lim_{n \rightarrow 0} \frac{\overline{\mathcal{Z}^n[\zeta(\boldsymbol{\rho})]} - 1}{n}. \quad (1)$$

With these preliminaries the free energy Eq. 1 can be evaluated via the standard Edwards-Anderson replica trick [7], where the replicated Hamiltonian \mathcal{H}_n is composed of the replicated elastic term

$$\frac{1}{2} \sum_{i=0}^n \iint d^2\boldsymbol{\rho} d^2\boldsymbol{\rho}' \mathcal{K}(\boldsymbol{\rho}, \boldsymbol{\rho}') u_i(\boldsymbol{\rho}) u_i(\boldsymbol{\rho}'),$$

where i is the index of the replica, the replicated constraint on the variable $B_i(\boldsymbol{\rho})$ that now reads

$$\frac{1}{2} \sum_{i=0}^n \int d^2\boldsymbol{\rho} g_i(\boldsymbol{\rho}) ((u_i(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho}))^2 - B_i(\boldsymbol{\rho})),$$

and finally of the replicated interaction and external “source” terms

$$\sum_{i=0}^n \int d^2\boldsymbol{\rho} V(B_i(\boldsymbol{\rho})) + \sum_{i=0}^n \int d^2\boldsymbol{\rho} \pi(u_i(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho})).$$

Since we now have Gaussian integrals over the variables $u_i(\boldsymbol{\rho}), \zeta(\boldsymbol{\rho})$ we can evaluate them explicitly, while the functional integrals over the auxiliary fields $B_i(\boldsymbol{\rho}), g_i(\boldsymbol{\rho})$ can be evaluated on the saddle-point level, with the *proviso* that there is no replica symmetry breaking. This constitutes the essence of the $1/d$ expansion.

After performing all the indicated integrations and taking the $n \rightarrow 0$ limit, the free energy can be obtained as a sum of the mean-field part ² and a fluctuation part. The mean-field part is

$$\mathcal{F}_0 = \int d^2\boldsymbol{\rho} \pi u_0(\boldsymbol{\rho}) + \frac{1}{2} \iint d^2\boldsymbol{\rho} d^2\boldsymbol{\rho}' \chi(\boldsymbol{\rho}, \boldsymbol{\rho}') u_0(\boldsymbol{\rho}) u_0(\boldsymbol{\rho}')$$

where the mean-field $u_0(\boldsymbol{\rho})$ is obtained via minimization of \mathcal{F}_0 with

$$\chi(\boldsymbol{\rho}, \boldsymbol{\rho}') = \mathcal{K}(\boldsymbol{\rho}, \boldsymbol{\rho}') + \delta^2(\boldsymbol{\rho} - \boldsymbol{\rho}') g(\boldsymbol{\rho}).$$

The fluctuation part of the free energy is concurrently obtained as

$$\begin{aligned} \mathcal{F} = & \frac{kT}{2} \int d^2\boldsymbol{\rho} \mathcal{G}^{-1}(\boldsymbol{\rho}, \boldsymbol{\rho}) g(\boldsymbol{\rho}) - \frac{kT}{2} \iint d^2\boldsymbol{\rho} d^2\boldsymbol{\rho}' \chi^{-1}(\boldsymbol{\rho}, \boldsymbol{\rho}') \mathcal{G}^{-1}(\boldsymbol{\rho}', \boldsymbol{\rho}) g(\boldsymbol{\rho}) g(\boldsymbol{\rho}') - \\ & - \frac{1}{2} \int d^2\boldsymbol{\rho} g(\boldsymbol{\rho}) B(\boldsymbol{\rho}) + \int d^2\boldsymbol{\rho} V(B(\boldsymbol{\rho})). \end{aligned} \quad (2)$$

On the $1/d$ expansion level the auxiliary fields contribute only at the saddle point. The saddle point equations are now obtained simply by minimizing Eq. 2 with respect to $B(\boldsymbol{\rho})$ and $g(\boldsymbol{\rho})$. We will not reproduce the general rather awkward form of these equations but will concentrate on a rather particular solution characterized by $u_0 = \text{const.}$ and $B = \text{const.}$, implying also $g = \text{const.}$. In addition to this we will limit ourselves to the conceptually most interesting case of vanishing external confining force, i.e. $\pi = 0$.

Assuming that the system is homogeneous in the $\boldsymbol{\rho}$ plane we can introduce the Fourier transforms of all the relevant quantities that allow us to write the mean-field equations in a rather simple form

$$u_0 \chi(\mathbf{Q} = 0) = u_0 g = 0. \quad (3)$$

The saddle point for B is obtained straightforwardly as

$$\frac{\partial V(B)}{\partial B} = \frac{1}{2} g,$$

while the saddle point for g can be derived in the form

$$B = u_0^2 + kT \sum_{\mathbf{Q}} \frac{\mathcal{K}(\mathbf{Q})^2}{\mathcal{G}(\mathbf{Q})(\mathcal{K}(\mathbf{Q}) + g)^2}.$$

This set of equations has two fundamentally different solutions describing the state of the elastic membrane interacting with a disordered substrate.

²Not to be confused with the mean-field approach introduced in [6]. The term mean-field is used here strictly as it pertains to the $1/d$ expansion.

1. a *hovering state*, with $u_0 \neq 0, g = 0$, characterized by

$$\frac{\partial V(B)}{\partial B} = 0 \quad \text{with} \quad B = u_0^2 + kT \sum_{\mathbf{Q}} \mathcal{G}^{-1}(\mathbf{Q}). \quad (4)$$

2. and a *pinned state*, with $u_0 = 0, g \neq 0$, characterized by

$$\frac{\partial V(B)}{\partial B} = \frac{1}{2}g \quad \text{with} \quad B = kT \sum_{\mathbf{Q}} \frac{\kappa(\mathbf{Q})^2}{\mathcal{G}(\mathbf{Q})(\kappa(\mathbf{Q})+g)^2}. \quad (5)$$

Obviously, in order to progress we have to assume a certain form for the quenched disorder correlation function. As a simplest approximation we take a spatially short range coupling $\mathcal{G}(\boldsymbol{\rho}, \boldsymbol{\rho}') = G\delta^2(\boldsymbol{\rho} - \boldsymbol{\rho}')$, implying $\mathcal{G}(\mathbf{Q}) = G$. Thus we have in the hovering state

$$\frac{\partial V(B)}{\partial B} = 0 \quad \text{with} \quad u_0^2 = B - B_c, \quad (6)$$

where we introduced $B_c = kT \sum_{\mathbf{Q}} \mathcal{G}^{-1}(\mathbf{Q}) = \frac{kT}{G} \frac{Q_{max}^2}{4\pi}$, that obviously depends on the upper wavevector cutoff in the Fourier space. The first of the above equations determines B as a function of the parameters of the DLVO potential (e.g. Hamaker constant, hydration interaction strength etc.). The second one gives the dependence of u_0 on these parameters.

In order to understand the physical nature of the two phases, we evaluate the average of the separation between the substrate and the membrane that can be obtained as

$$S^{-1} \int d^2 \boldsymbol{\rho} \overline{\langle u(\boldsymbol{\rho}) - \zeta(\boldsymbol{\rho}) \rangle} = u_0.$$

Clearly u_0 quantifies the disorder averaged separation between the membrane and the substrate. For a finite u_0 the membrane hovers a finite separation away from the substrate. In order to characterize the hovering state further we evaluate the average square of the deviation from a unit normal to the membrane in the z direction given to the lowest order as $\delta \mathbf{n}(\boldsymbol{\rho}) \approx \nabla_{\perp} \cdot u(\boldsymbol{\rho})$,

$$p^2 = S^{-1} \int d^2 \boldsymbol{\rho} \overline{\langle \delta \mathbf{n}^2(\boldsymbol{\rho}) \rangle} = \frac{kT}{2G} \frac{g^2}{\sum_{\mathbf{Q}} \frac{Q^2}{(\kappa(\mathbf{Q}) + g)^2}} = \frac{kT}{16\pi} \frac{g}{G K_c}. \quad (7)$$

Thus in the hovering state with $g = 0$ not only is the membrane decoupled from the substrate and hovers above it, but is also flat on the average since the mean disorder averaged squared deviation from the normal, p^2 , equals zero at a finite separation u_0 (see figure). Obviously the hovering solution exists only for $B > B_c$. The hovering line in the “phase diagram” thus ends at the value of the interaction parameters where the solution of $\frac{\partial V(B)}{\partial B} = 0$ also satisfies $B = B_c$. u_0 thus behaves as an order parameter of a second order phase transition, and B behaves as the temperature.

Furthermore the surface density of the adhesion free energy (U) in the hovering state is given by

$$U = \min \left\{ \frac{\mathcal{F}}{S} \right\} = V(B) = V(u_0^2 + B_c).$$

This obviously differs from the standard secondary minimum of the DLVO theory, determined from $\frac{\partial V(u_0)}{\partial u_0} = 0$, with $U = V(u_0)$. The free energy in the hovering state is thus not given by the value of the DLVO potential at the minimum $V(u_0)$, but at a (much smaller) value of $V(u_0^2 + B_c)$, since V is a decreasing function of its argument above its minimum.

In the hovering state the membrane is obviously in close proximity (“contact”) of the substrate only for a fraction of its total surface area. This effective contact area (S_c) can be estimated [6] from

$$\frac{S_c}{S} = \frac{V(u_0^2 + B_c)}{V(u_0^2)}.$$

In view of the discussion presented above, this ratio is smaller than one if V is a decreasing function of its argument above its minimum value.

For the pinned state, with $\mathcal{K}(\mathbf{Q}) = Q^4 K_c$, we obtain the following expression to the lowest order in the wavevector cutoff Q_{max}

$$\frac{\partial V(B)}{\partial B} = \frac{1}{2}g \quad \text{with} \quad B = B_c - \frac{3kT}{16G} \sqrt{\frac{g}{K_c}},$$

where B_c is defined in the same way as in the hovering state. The adhesion free energy in the pinned state, defined in complete analogy with the hovering state, is given by

$$U = V(B) + \frac{kT}{4\pi G} \frac{K_c}{K_c} \left(\frac{g}{K_c} \right)^{\frac{3}{2}} = V(B) + \frac{16^3}{4\pi 3^3} \frac{K_c G^2}{(kT)^2} (B_c - B)^3.$$

In the pinned state the membrane is thus coupled to the substrate and follows it closely, being always in its close proximity since $u_0 = 0$ (see figure). It thus exhibits a very corrugated configuration. This follows again from Eq. 7 since in the pinned state $p^2 \neq 0$. We note that for non-zero external driving force π the system is always in the pinned state.

The adhesion energy in both states is nowhere in general equal to its DLVO counterpart. Both, the hovering as well as the pinned states carry in the free energy the signature of the substrate disorder in the height-height correlations. Only in the limit of vanishing disorder, or in the language of our model as $G \rightarrow \infty$, does the hovering state approach the DLVO secondary minimum in a continuous fashion, while the pinned state simply disappears.

In order to gain further insight into the nature of the hovering and the pinned states we investigate the phase diagram for a particular typical choice of the DLVO interaction

potential augmented by the Helfrich undulation interaction. For the sake of simplicity we assume that the DLVO part is given by the sum of the hydration and van der Waals interactions while the Helfrich interaction is assumed to have the same form as between a flexible membrane and a flat substrate [1, 2], thus

$$V(u) = Ae^{-u/\xi} - \frac{H}{12\pi u^2} + \frac{6\pi^2(kT)^2}{256K_c u^2} \quad (8)$$

where A is the magnitude and ξ the range of the hydration interaction, and treat the Hamaker constant H as a variable tuning parameter. The above form of the total interaction energy between a membrane and a substrate would be strictly valid only for a membrane fluctuating near a flat substrate. However Swain and Andelman note [6] that the form of the Helfrich interaction should not be far off from the one in the above expression even for a rough substrate. We assume this is the case when we analyze the phase diagram for a membrane near a disordered substrate. This assumption would however have to be tested via a more sophisticated and hopefully more accurate approach.

Without the disorder the interaction potential Eq. 8 leads to an unbinding transtion at the critical value of the Hamaker constant equal to $H_c = \frac{72\pi^3(kT)^2}{256K_c}$. When H approaches this value the secondary DLVO minimum is displaced towards infinity and we have a continuous unbinding of the membrane. Adding disorder to this scenario we instead obtain a modified phase diagram as presented on the figure. There is now a window corresponding to the hovering state (the former DLVO secondary minimum) in between the pinned and the unbound state of the membrane. The dimensions of this window depend on the value of \mathcal{G} that characterizes the intensity of the substrate disorder. In the limit of no disorder $\mathcal{G} \rightarrow \infty$ with $B_c \rightarrow 0$ the hovering window is expanded to the whole axis $H > H_c$ and is tranformed back into the standard DLVO secondary mimimum.

The disorder usually does not figure in the theories of membrane substrate interactions. The present work is basically a plea for a change of this perspective. There obviously exist phenomena, where ignoring the disordered nature of the substrate does not, even qualitatively, lead to the correct physical picture. In this sense the DLVO theory has to be ammended.

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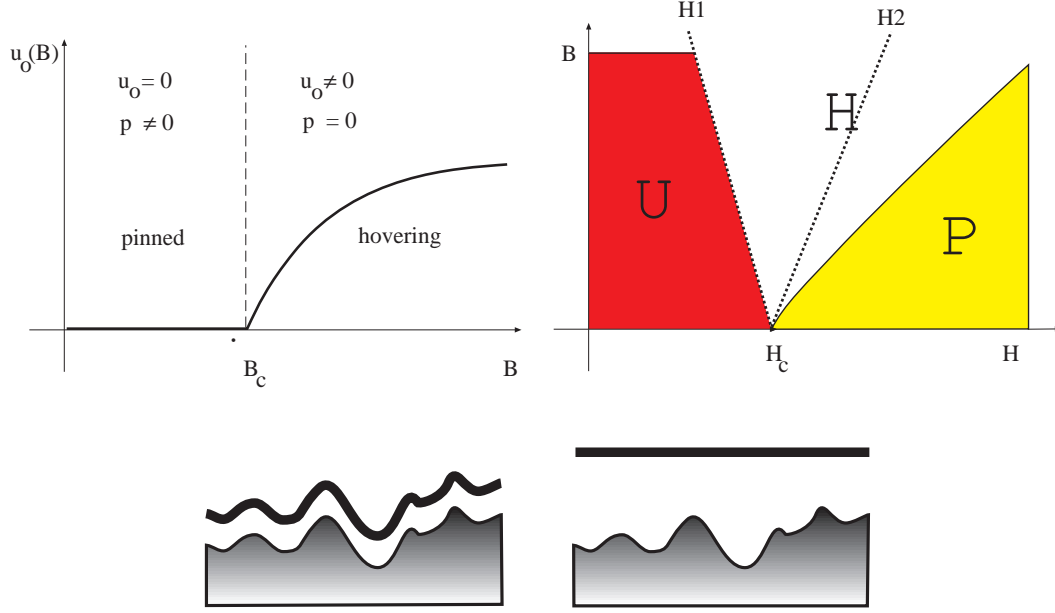


Figure 1: Upper left: Schematic dependence of u_0 on the auxiliary field B . The hovering state exists only for $B > B_c$. The critical value B_c depends on the disorder characteristics of the substrate and the microscopic wavevector cutoff. The hovering - pinned transition is obviously second order in B , which thus plays the role of the temperature. Upper right: Schematic phase diagram of a membrane as a function of the Hamaker coefficient; $V(u)$ is assumed to be equal to the sum of hydration, van der Waals and Helfrich terms Eq. 8. The substrate disorder introduces a hovering (H) state window into the phase diagram, located between the pinned (P) and the unbound (U) phases. Two possible (H-U) boundaries are indicated by the H1 and H2 lines. The size of this window depends on the strength of the Hamaker coefficient and the value of G , characterizing the disorder effects. In the case of no disorder ($B \rightarrow 0$) the critical value of the Hamaker coefficient H_c marks the unbinding transition of the membrane. Bottom: A schematic representation of the hovering (H) and the pinned (P) state of the membrane in proximity of a disordered substrate. The hovering state is characterized by a slowly varying average separation between the membrane and the substrate that does not follow closely the local corrugations of the substrate. In the pinned state however, the membrane follows closely the asperities of the substrate.